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REVIEW OF SOVIET WORK IN THE FIELDS OF CHEMISTRY AND CHEMICAL TECHNOLOGY DONE BY 1951 STALIN PRIZE LAUREATES

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N. A. Preobrazhenskiy has carried out extensive investigations on the synthesis of alkaloids, vitamins, and other naturally occurring compounds. His work on the constitution and synthesis of alkaloids of the pilocarpine group extends over a period of 25 years. He definitely established the constitution of pilocarpine and of its decomposition products by the analytical as well as the synthetic method, investigated the stereochemistry of pilocarpine alkaloids, and accomplished a total synthesis of pilocarpine as well as of all of its theoretically possible stereoisomers. A number of homologs and analogs of these stereoisomers was also synthesized by him. He developed a method which is suitable for the preparation of pilocarpine from the practical standpoint. Clinical investigation of synthetic pilocarpine showed that it is as effective therapeutically as the natural alkaloid. The synthetic, optically active stereoisomer proved to be identical with the natural alkaloid.

Work published by Preobrazhenskiy and collaborators describes the synthesis and properties of all principal natural alkaloids of this group, i.e., d-pilocarpine, d-isopilocarpine, d-pilocarpidine, d-isopilocarpidine, pilosturine, and more than 50 of their isomers, homologs, and analogs. By modifying the molecule of pilocarpine, it was possible to synthesize a compound which is physiologically more active than pilocarpine.

The second group of alkaloids, of which the synthesis was accomplished by Preobrazhenskiy, are alkaloids of ipecac usaba. The constitution of emetine had not been clarified until recently and was definitely established only on the basis of synthetic work done by this investigator. Preobrazhenskiy synthesized not only racemic emetine, but also the l-isomer which is identical with

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the natural alkaloid. The synthesis accomplished by him is original and represents the result of investigations in the field of isoquinoline alkaloids extending over many years.

Besides working on the alkaloids mentioned above, Preobrazhenskiy carried out investigations on the tropane derivatives cocaine and scopolamine; arecoline; the purine bases theophylline, caffeine, and theobromine; histamine; etc. In addition to working on alkaloids, he conducted extensive investigations in the field of vitamins. On the basis of the investigation in question, a number of procedures used in the vitamin industry was developed.

As early as 1926, Academician I. I. Chernyayev discovered the phenomenon of transinfluence in complex compounds. This constitutes one of the most important discoveries in this particular field made during the past 25 years; it permits the synthesis of new complex compounds and development of new chemical methods for determining their structure. Investigations carried out by Chernyayev in 1949 - 1951 were concerned with checking, confirming, and introducing further precision into his original results. On the basis of the newly discovered principle, he succeeded in synthesizing five optically active geometric isomers of tetravalent platinum derivatives, which contain five different intrasphere substituents. In work done abroad, more than two isomers of this type were never synthesized. Chernyayev also synthesized and investigated a number of important isomers of diaminodinitrocompounds of tetravalent platinum. His work on complex compounds is not only of outstanding theoretical interest but also of great importance from the economic standpoint.

Professor Yu. A. Gorin-Hast's work dealt with the catalytic conversion of ethyl alcohol into butadiene. The catalyst used for this purpose was proposed in 1928 by the founder of the USSR synthetic rubber industry, Academician S. V. Lebedev, but the mechanism of the reaction remained unknown. Gorin-Hast's work established the fine mechanism of this reaction and elucidated the role which individual components of the catalyst play in the conversion. According to the reaction scheme set up by him, an initial dehydration of ethyl alcohol into acetic anhydride takes place. The acetic anhydride is then condensed into croton aldehyde, which in turn is reduced to crotonyl alcohol. In the final step, crotonyl alcohol is dehydrated, forming butadiene. After establishing this general mechanism, Gorin-Hast proved that it also applies to other alcohols besides ethanol, and furthermore, that it is also valid for binary mixtures of alcohols and mixtures of alcohols with carbonyl compounds. The relationships discovered in the course of this work permit steering of the reaction in the desired direction by selecting suitable initial alcohols or mixtures of alcohols and carbonyl compounds (aldehydes or ketones), so that the required diethylenic hydrocarbons are obtained. The reactions leading to by-products in the course of the catalytic conversion of ethanol were also clarified. Work on the subject done by Gorin-Hast in 1935, established the priority of USSR science in discovering the reaction mechanism in question.

Gorin-Hast's work, besides being a valuable contribution to the knowledge of reactions taking place under the influence of mixed catalysts, is of great practical importance to the rubber industry.

The work of G. Kh. Kamay, Professor of the Chemicotechnological Institute imeni S. M. Kirov, at Kazan', is based on the reaction of trialkyl esters of phosphorous acid with alkyl halide, discovered by A. Ye Arbuzov and known as the Arbuzov rearrangement. Kamay is investigating the possibilities of applying this reaction to the synthesis of arsenic derivatives. He also applied another method of synthesizing organophosphorous compounds, which is based on the reaction of organic halogen compounds with metal derivatives of dialkyl phosphites. Kamay has synthesized and characterized more than 20 new representatives of phosphorous-carboxylic acids and approximately the same number

of amides of these acids. He further succeeded in showing that secondary haloarsines react with trialkyl phosphites or metal derivatives of dialkyl phosphites in the same manner as alkyl halides. The products of the reaction are then esters of cacodyl phosphonic acid, a class of phosphorus-arsenic organic compounds which had not been previously described. Twelve compounds of this class have been synthesized by Kamay. To establish whether or not alkyl esters of arsenous acid undergo the Arbuzov rearrangement under the action of alkyl halides, Kamay, using the known method of synthesizing trialkyl phosphites, prepared several representatives of the series of trialkyl arsenites and showed that the latter do not react with alkyl halides. In the series of arsenic organic compounds, Kamay also synthesized four trialkylarsines having the general formula R_2AsCH_2COOR.

Kamay has accomplished extensive work which is very interesting from the theoretical standpoint. He synthesized and characterized about 100 new phosphorus and arsenic organic compounds belonging to the most diverse types.

The work done by A. T. Vagramyan, who is head of the laboratory, Institute of Physical Chemistry, Academy of Sciences USSR, is summarized in the monograph "Electrodeposition of Metals," published by him in 1950. Vagramyan has shown that the polarization which is observed during the electrodeposition of metals cannot be explained either by the delayed discharge of metal ions or the difficulties which arise in connection with the formation and growth of crystal nuclei. Using a newly developed method for measuring the growth of single crystals, he demonstrated that the number of crystalline nuclei which forms depends principally on the degree of polarization of the electrode and the rate of passivation. He also proved that many experimental data on the degree of polarization that were obtained by the usual method do not reflect the actual dependence between the current density and the degree of polarization, because changes in the magnitude of the active surface of electrodes bring about changes in the true current density. In connection with this, Vagramyan worked out a very rapid automatic method of taking polarization curves in which the results are not affected by changes in the surface of the electrodes. This method permits one to apply high current densities and avoid concentration polarization.

Vagramyan further showed that the overvoltage which is observed during the electrolytic deposition of silver is caused by concentration polarization and is not connected with the necessity of expending additional energy to bring about formation of crystal nuclei, as had been assumed by some investigators. Of great interest are Vagramyan's investigations on the effect of surface active compounds. He came to the conclusion that a uniform deposit of the metal is formed whenever a continuous, stable film of an adsorbed surface active compound is present. The metal is deposited unevenly in various parts of the electrode in cases when there is no continuous film. During the course of electrolytic deposition, there is competition between two oppositely directed processes, passivation and metal deposition.

G. M. Panchenkov, Professor of the Moscow Petroleum Institute, has been active in the field of the theory of viscosity of liquids. He formulated the simplest assumptions pertaining to the mechanism of transmission of an impulse from one layer of a liquid to another. These assumptions permitted him to derive a formula expressing the dependence of viscosity on temperature, pressure, and the molecular constants of a liquid. He based his theory on the concept that a quantity of motion is transmitted by molecules of a liquid during the temporary joining of these molecules into pairs due to the force of cohesion and assumed that the number of these cohesions is proportional to the number of pair collisions between the molecule under consideration and others. Panchenkov demonstrated that the equation formulated by him expresses accurately the temperature dependence of the viscosity of liquids which are very different in

nature (hydrocarbons, alcohols, organic acids, halogenated hydrocarbons, salt melts, liquefied gases, etc). Calculation by means of this equation of temperature dependence of the viscosity of liquids, coordination numbers, and molecular radii indicated the possibility of calculating absolute values of viscosities of liquids on the basis of the equation in question. When certain assumptions are made, Panchenkov's equation is transformed into the temperature-viscosity equations proposed earlier by A. I. Bachniskiy, Ya. I. Frenkel', etc.

Using Panchenkov's equation and taking into consideration changes in the density and binding energy of molecules of a liquid resulting from changes in pressure, one may calculate changes of viscosity with pressure. This equation can also be used for calculating the viscosity of liquid mixtures. Thus, Panchenko's theory may be regarded as an approximate, simplified scheme which correctly represents phenomena of the viscosity of liquids.

N. V. Belov, corresponding member, Academy of Science USSR, has done research on the atomic structure of crystals. Belov's work in this field represents an extension of his ideas on the application of the concept of densest sphere packing to disentangling of complicated crystal structures (particularly those of minerals), as well as to the explanation of the physical and chemical characteristics of these crystals (especially phenomena which are observed in connection with the joint formation of crystals, such as twinning, etc). In the course of this work, much attention has been paid to the nature of inclusion of small quantities of rare elements into the lattices of common minerals. The principle of densest packing and its applications have been already expounded in Belov's widely known book, Structures of Ionic Crystals and Metal Phases, which was published in 1947. In other publications by Belov, three new and complicated silicate structures have been deciphered. The presence of a formerly unknown type of silicon-oxygen radical $Si_{12}O_{13}$, which has the shape of a double-layered /literally two-story/ ring with an axis of symmetry of the sixth order, was established by him in milarite. As far as ramsayite is concerned, which has an over-all orthosilicate formula Si:O = 4 1/2, he proved the presence in it of a metasilicate radical with the pyroxene pattern $(SiO_3)_\infty$. One third of the oxygen atoms is not included in the silicon-oxygen pattern but connects the atoms of titanium with those of sodium. In tourmaline, the presence of a two-layered ring similar to that found in milarite was established, except that the ring in this case has a trigonal symmetry. One of the layers is composed of silicon atoms, the other of aluminum and boron atoms, in consequence of which the pronounced polar properties of the mineral result. In deciphering this structure, Belov was compelled to enter into a controversy with M. J. Burger the prominent US crystallographer. The fact that Burger was wrong is apparent if one compares the atom coordinates in the first version of his work with the coordinates which he used in a later version, after familiarizing himself with Belov's work. Furthermore, Belov attempted to explain the well-known mineral-forming action of fluoride and hydroxyl ions using the principle of the densest packing of atoms. The theory in question is also applicable to the study of the sequence in which minerals crystallize from magma.

In the course of work on the latent photographic image, Professor Ye. A. Kirillov, Odessa State University imeni I. I. Mechnikov, discovered and investigated the fine structure of the absorption spectrum of photochemically colored silver halide. As a result of his investigations, Kirillov arrived at the conclusion that the absorption bands corresponding to the fine structure must belong to centers formed by silver which is dispersed in the form of atoms and composes particles consisting of a small number of atoms weakly bound to the crystal lattice and located principally on the surface of the crystals. To check the accuracy of this concept on the nature of centers responsible for the fine structure, special experiments were carried out with thin polycrystalline layers of silver chloride and silver bromide that were colored by sputtering silver metal on to their surface in vacuum. One may expect that if the centers

responsible for the fine structure are composed of only a few atoms of silver, these centers will be destroyed under the action of light that is within their absorption range. Spectroscopic measurements actually showed that the centers responsible for the fine structure are destroyed under the action of light of appropriate wave length, with the maximum effect corresponding to wave lengths that coincide with the maxima of the centers' absorption.

In other investigations, Kirillov showed that in complete accordance with contemporary views on the subject, destruction of a center consisting of a few silver atoms is accompanied by an internal photoeffect. The series of investigations carried out by Kirillov opens a direct path to the investigation of the latent image, which is the cardinal problem of the theory of the photographic process.

Professor V. N. Tsvetkov, Leningrad State University imeni A. A. Zhdanov, has investigated the structure and properties of high-molecular compounds. In the course of his work, Tsvetkov developed the application to solutions of polymers and various systems related to them (sols, organic chain molecules, and oils), of diverse optical methods which permit clarification of the structure of chain molecules, their swarms, and sol micelles i. e., determination of their size, shape, and some properties. Tsvetkov subjected to a many-sided study of phenomena of double refraction in such systems, both in flow and in an ultrasound field, using the data obtained in these measurements to investigate polymerization kinetics and to solve the problem of determining the rigidity and relaxation of macromolecules of polymers and other long chain molecules. By combining data on dynamic and acoustic double refraction, Tsvetkov was able to determine the relaxation time of a number of high-molecular species.

The method of a rotating magnetic field developed by Tsvetkov permits analysis of colloidal systems and determination of the magnetic properties of colloidal particles. For instance, with the use of this method, he detected the paramagnetism of graphite particles, which is due to the adsorption of oxygen by graphite. A significant result of Tsvetkov's work is a new method developed by him for the study of the diffusion polymers in solution. This method involves the use of Academician A. A. Lebedev's polarization interferometer. Application of the method in question permitted Tsvetkov to measure the rate of diffusion at concentration differences amounting to 0.02-0.03%. He also established the existence of the highly unique phenomenon of increase of the rate of diffusion with concentration. The possibility of determining accurately the values of diffusion constants in very dilute solutions, where interaction between molecules of the polymer is actually absent, represents an important extension of experimental methods for the investigation of polymers.

G. A. Smolenskiy, N. A. Toropov, and A. I. Borisenko, scientific associates of the Institute of Silicate Chemistry, Academy of Science USSR, have investigated the physical and chemical properties of seignettoelectric /piezoelectric/ substances and ferrites. For several years, they conducted research on physicochemical systems formed by oxides of iron, titanium, circonium, and tin with oxides of divalent metals. In the course of this work, the optimum conditions for the synthesis of a number of solid solutions, mainly those belonging to the crystalline phases of the spinel and perovskite structures, were established and the magnetic and seignettoelectric properties of the systems in question determined. A skillful combination of methods of thermochemistry, X-ray analysis, and microscopy enabled these investigators to establish a number of very important relationships having a bearing on the limits within which mixed crystals exist, i. e., to discover that divalent oxides are soluble in tricomponent ferrites and that there is formation of solid solutions of the first and second type in such systems. The work in question led them to the discovery of new, nonmetallic magnetic substances,

which exhibit a high resitivity, a high magnetic permeability, and low losses at audio and radiotechnical frequencies, a set of properties which is very important for practical applications.

The work of Smolenskiy, Isropov, and Borisenko considerably expanded our knowledge of seignettoelectric substances. They demonstrated that barium titanate /a piezoelectric substance which is very useful from the practical standpoint/ which was discovered by B. M. Vul, is one of the rather numerous seignettoelectric substances having a structure of the perovskite type. They also discovered new seignettoelectric substances. It has been shown that in seignettoelectric substances, there is spontaneous alteration of the volume at temperatures below the Curie point. Depending on the nature of the seignettoelectric substance, the change in volume may assume either a positive or negative value. From this, Smolenskiy and his coworkers drew the correct conclusion that within a system of solid solutions, one may obtain seignettoelectric substances possessing a zero electrostriction and, therefore, having a very high dielectric permeability. This conclusion was confirmed by experimental results: in complete accordance with this principle, a new group of seignettoelectric substances having a high dielectric permeability was obtained.

N. M. Sisakyan, head of laboratory, Institute of Biochemistry imeni A. N. Bakh, Academy of Science USSR, published in 1951 his monograph "Enzyme Activity of Protoplasma Structures," which is devoted to one of the cardinal problems of contemporary biochemistry. In the course of the work described by him, Sisakyan has solved, both theoretically and experimentally, many important problems in this field. On the basis of extensive experimental data obtained by him with the aid of modern methods (electron microscopy, chromatography, etc.), he succeeded in clarifying the biological and biochemical significance of the structural heterogeneity of protoplasm, as well as in demonstrating the alteration and effect of the structures in question in the course of the process of metabolism.

Sisakyan's monograph presents new data on the character of the changes which the structure of chloroplasts, chromoplasts, and leucoplasts undergoes during the life cycle of the organism. Application of histochemical and electron-microscopic methods led to elucidation of the structure of chromoplasts and leucoplasts and indicated that plastids are composed chiefly of lipoproteids. Chromatographic investigation of the amino acid composition of plastids disclosed that their proteins are composed of 17 amino acids. It was also established that plastids are very rich in diverse catalysts, thus actually constituting depots of enzymes.

Sisakyan obtained new essential data on the enzyme activity of chloroplasts. It is known that photosynthesis consists of photochemical stages in which chlorophyll participates and dark reactions which take place as a consequence of the directing effect of enzymes. However, the nature of the enzymes taking part in photosynthesis had not been definitely established until recently.

As a result of extensive investigations, the presence of 13 enzymes was established in chloroplasts. Seven of them were discovered by Sisakyan. The following enzymes were found in chloroplasts and investigated: peroxydase, polyphenoloxydase, cytochromoxydase, phosphorylase, phosphoglucomutase, proteases, and mutases. Clarification of the fact that the main quantity of oxidation enzymes is bound to plastids must be considered very important. Sisakyan was the first to establish the presence of enzymes in chromoplasts and leucoplasts. The high enzyme activity of chloroplasts definitely indicates that a number of enzymes contained in them may participate in the reactions of photosynthesis.

As far as inventions and radical improvements of production methods in various fields are concerned, the following achievements may be noted. Docent A. M. Minkevich, Moscow Steel Institute, has developed highly efficient chemico-thermal methods of steel treatment and introduced them into practice. A team composed of M. A. Malin, S. M. Markevich, N. T. Man'ko, A. A. Serov, I. A. Migalovskiy, A. A. Venchegdt, G. M. Maganova, A. A. Vvedenskiy, and S. P. Arkharov has developed and introduced a new method for the production of alcohol. Ye. A. Ivanov, O. V. Korsunskiy, V. A. Kuvachinskiy, Ye. A. Postovskaya, I. N. Poshidayev, A. N. Shabuyev, A. P. Shestov and I. L. Lipkin introduced radically new procedures for the production of dyestuff intermediates. M. A. Krupyshev, N. A. Glagolova, F. P. Filimonov, scientific associates of the All-Union Scientific Research Institute of Synthetic Rubber imeni Academician S. V. Lebedev and A. M. Zenitov and M. A. Kyznezanov, engineers, developed and introduced into industrial production a new type of synthetic rubber. A group of engineers working under the direction of S. V. Shutskiy introduced into practice a method for the industrial production of a new chemical product. A group of metallurgical engineers headed by N. S. Scliverstov introduced a new industrial method of obtaining a metal.

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